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ANION-EXCHANGE SEPARATION OF NEPTUNIUM FROM URANIUM AND THORIUM IN BASIC SOLUTION

by

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ABSTRACT

The anion-exchange behavior of neptunium, uranium, plutonium, thorium, and several accompanying elements has been studied in an aqueous tetramethylammonium hydroxide (TMAH) medium and in this same basic medium containing various complexing agents. It has been found the neptunium in the +5 oxidation state is not retained by Dowex-1x8 resin from slightly basic TMAH-citrate solution and is readily separated from uranium and thorium, which are retained by a column of this resin.

I. INTRODUCTION

Several techniques available for the separation and purification of neptunium appear in the literature. Among these are precipitation methods,¹ solvent extraction,^{2,3} and ion exchange.^{4,5}

Most methods concerned with separation of neptunium employ acid solution,^{3,4} but a recent study of neptunium by Cohen and Fried⁶ suggested the use of ion exchange in a basic medium. Using electromigration, chemical-behavior studies, and ion exchange, these authors show that Np(V) exists as an anion in basic media. In particular, they found that Np(V) was relatively soluble in tetramethylammonium hydroxide (TMAH) solution (0.5M),* and from this medium the Np(V) was retained on an anion exchanger. Because of this behavior of neptunium in basic (TMAH) media, an investigation was undertaken to study possible separations from accompanying actinides and other elements. Batch-distribution coefficients (K_D) were determined for U(VI), Th(IV), Np(VI), Pu(IV), and Np(V) in pure TMAH solutions and in various eluting agents at both pH 8 and 10. Some of the agents investigated include TMAH alone, citrate, tartrate, $\text{TMA}^+ \text{CL}^-$, and combinations of these agents. A solution containing tetramethylammonium citrate (0.5M in citrate) and adjusted to pH 8 with a slight excess of TMAH gave a good separation of Np(V) from U(VI) and Th(IV) on a Dowex-1x8 resin column. Further investigation showed a separation of U(VI) from

*Up to 0.5M Np(V) in 1M TMAH (unpublished recent data).

Th(IV) in the system 0.9M TMAH, 0.1M citrate. Several other elements (Mn, Al, Pb, Ni, Zn, Cu, Co, Fe, and Pu) were investigated by batch and column work in the TMAH-citrate (pH 8) eluent and were expected to be generally representative of the majority of elements that could be present as impurities.

II. EXPERIMENTAL PROCEDURES

All chemicals used were of the reagent grade, except the tetramethylammonium hydroxide. The latter (of a purified grade) was dissolved in boiled column water to make a 3M stock. Solid $\text{Ba}(\text{OH})_2^*$ was added to remove any CO_3^{2-} . The BaCO_3 and $\text{Ba}(\text{OH})_2$ were filtered off after 24 hr. The TMAH stock thus made was diluted to make other concentrations.

Reagents were prepared as TMAH salts of citrate, chloride, carbonate, ethylenediaminetetracetate, tartarate, succinnate, malonate, oxalate, glycolate, salicylate, 5-sulfosalicylate, α hydroxyisobutyrate, phthalate, and acetylacetonate. These were prepared at concentrations of 0.1M and 0.5M in the organic acid ion.

$^{233}\text{U}(\text{VI})$, $^{230}\text{Th}(\text{IV})$, and $^{238}\text{Pu}(\text{IV})$ were obtained from stock HCl solutions.

Al(III), Ni(II), Zn(II), Cu(II), Fe(III), and Co(II) chlorides were dissolved in water at 20 mg/ml. $\text{Pb}(\text{NO}_3)_2$ at 20 mg Pb/ml in water was also used.

Manganese-54 tracer was obtained from acid stock solutions.

To prepare the Np(V) stock solutions, neptunium was evaporated to dryness three times in concentrated HNO_3 solution and redissolved in 0.5-1M HCl. Sodium nitrite was added to reduce Np(VI) to the bright green Np(V). Ammonium hydroxide solution was then added to precipitate the green Np(V) hydroxide, which was centrifuged and washed three times with deionized water. Addition of 1M TMAH dissolved the precipitate to form the anionic Np(V) solution. In this manner, stock solutions of 44 and 38.7 mg/ml were prepared.

All TMAH-complexing agent solutions were prepared by neutralizing the appropriate amount of TMAH with the complexing agent to give a pre-determined salt concentration. Excess TMAH was then added to adjust the solution to pH 8 or 10.

Dowex-1x8, 100-200 mesh, was prepared as a slurry directly from the bottle and transferred to the column in the chloride form. For batch

*Solubility of barium in 3M TMAH is approximately 1 μg of barium per milliliter.

work, a solution of NH_4OH was added to the resin slurry to put it in the hydroxide form, after which all free NH_4^+ was washed out with water.

III. APPARATUS

Columns were glass tubes 6×0.5 cm with an attached reservoir of 7×0.8 cm. The slurry was transferred into a column and allowed to settle uniformly onto a quartz-wool plug to a height of 3.3 cm.

For batch measurements, 13-ml screw-cap centrifuge tubes were used and mixed on a rotator that could accommodate 22 tubes.

A. Assay Techniques

The ^{233}U , ^{238}Pu , ^{230}Th , and ^{237}Np were counted on a flow-proportional alpha counter.

The ^{54}Mn was analyzed with a multichannel gamma-ray analyzer using the 0.835-MeV peak with a NaI crystal. The other metals (listed in Table I) were determined spectrographically.

TABLE I. K_D Values for Other Metals
Studied in 0.5M Citrate + 0.015M
Free TMAH (pH 8)

Metal	K_D	Metal	K_D
Al(III)	8	Zn(II)	14
Co(II)	11	Pb(II)	<1
Cu(II)	12	Mn(II)	<10
Ni(II)	2	Fe(III)	~5

B. General Procedure

1. Determination of Batch Distribution Coefficients

The resin was converted in large volumes, as described at the end of Section II, to the ^-OH cycle with NH_4OH . The resin content was determined by weight difference after drying at 90°C overnight to be 0.45 g of dry resin per milliliter of slurry, and the interstitial aqueous volume determined by difference to be 0.5 ml per milliliter of resin slurry.

Two milliliters of a TMAH or TMAH-complexing agent solution (listed in Table II) were spiked with at least 10^6 counts/min of alpha activity from one of the following tracers: $^{233}\text{U(VI)}$, $^{230}\text{Th(IV)}$, $^{238}\text{Pu(IV)}$, $^{237}\text{Np(VI)}$,

and $^{237}\text{Np(V)}$. The tracer aliquots were made neutral with TMAH prior to addition. Each tracer solution was loaded into a centrifuge tube containing 1 ml of resin slurry, which was preequilibrated with the same TMAH or TMAH-complexing agent solution. The tubes were capped and shaken overnight. The K_D values* for each element were determined by comparing an assay of an equivalent control solution prepared without resin to the assay of the tracer solution equilibrated with the resin, corrected for background and interstitial volume of the resin.

TABLE II. Batch Distribution Coefficients

Complexing Media:	U(VI)		Th(IV)		Np(VI)		Pu(IV)		Np(V)	
0.1M TMAH:	208		>500		>500		125		242	
1.0M TMAH:	22		350		40		210		12	
3.0M TMAH:	9		527		24		7		3	
	pH 8	pH 10	pH 8	pH 10	pH 8	pH 10	pH 8	pH 10	pH 8	pH 10
0.1M Citrate	229	38	1032	707	754	387	489	99	379	280
0.5M Citrate	125	10	178	73	50	67	41	24	11	14
0.1M TMA ⁺ CL ⁻	262	61	1000	1402	250	673	561	586	2007	719
0.5M TMA ⁺ CL ⁻	77	9	403	1457	110	162	18	94	80	17
0.1M Tartarate	259	126	1187	1830	968	3562	146	22	1072	694
0.5M Tartarate	77	27	410	231	311	331	152	148	77	71
0.1M (TMA) ₂ CO ₃	6	579	114	6813	1681	896	586	1564	125	589
0.5M (TMA) ₂ CO ₃	201	200	501	739	826	328	84	114	89	76
0.5M TMA ⁺ A ₂ C ₂ AC ⁻ + 0.015M TMAH	-	-	-	-	-	-	1	2	8	2

A₂C₂AC⁻: acetylacetonate.

(TMA)₂CO₃ concentration given in terms of CO₃⁼.

The solutions of Zn, Pb, Co, Cu, Fe, and Al were taken down to near dryness and then taken up in 0.5M citrate + 0.015M free TMAH (the concentration of free TMAH was determined by titration with standardized HCl and cresol red indicator) and loaded onto a resin pretreated with the same solution. Controls were prepared, and K_D values were determined for each element from the difference between what was initially added and what remained in solution, both determined spectrographically.

2. Effect of Complexing Agents

Several complexing agents used in this investigation were selected on the basis of their ability to prevent precipitation of Fe⁺³, La⁺³, Th⁺⁴, Bi⁺³, Sn⁺⁴, and Zr⁺⁴ in basic (TMAH) media. In each case, 5-10 mg of the element were added to a basic solution (pH > 9) containing the organic agent in 0.1 to 0.5M strength. (See Table III.)

* K_D is defined as the amount of an element in milligrams or activity units per gram of resin divided by the milligrams or activity units of the element per milliliter of solution in equilibrium with the resin.

TABLE III. Effect of Various Agents on Solubility of Selected Elements in Basic Solution (pH > 9)

Complexing Acid	Fe ⁺³	La ⁺³	Th ⁺⁴	Bi ⁺³	Sn ⁺⁴	Zr ⁺⁴
Succinic	P ^a	P	P	P	S ^a	P
EDTA	S	S	S	S	S	S
Malonic	P	P	P	P	S	S
Glycolic	S	P	S	P	S	S
Oxalic	P	P	P	P	S	S
After 20 min						
Salicylic	S	P	P	P	S	S
5-sulfosalicylic	S	P	P	P	S	S
Tartaric	S	S	S	S	S	S
Citric	S	S	S	S	S	S
α -hydroxy-iso-butyric	S	P	P	P	S	S
Phthalic	S	P	P	P	S	S
Malic	S	P	S	S	S	

^aS = soluble; P = precipitates.

3. Column Operation

The resin prepared as a slurry was transferred to the column, rinsed with 1.0M TMAH and then 0.1M TMAH. There were two general modes of operation: (1) The resin in the OH⁻ form was spiked on individual runs with uranium, plutonium, or thorium tracers from slightly basic solutions (freshly prepared) and, in the case of Np(V) and (VI), from its 1M TMAH solution. Following a 0.1M TMAH rinse, the eluting agent under investigation was passed through the column at 0.25-0.30 ml/min. Fractions were collected in 2- or 5-ml portions and assayed to determine the elution volume at the maximum concentration of the element. From this elution volume and the column size in grams, the K_D was calculated. (2) The resin was pretreated with the intended eluting agent, the tracers were absorbed from the same eluting-agent solution, and the procedure above followed.

In spite of a fairly high distribution coefficient (K_D > 500), Np(V) in pure TMAH solution is not rapidly adsorbed by Dowex-1x8 resin. Therefore, when it is desired that Np(V) be retained from pure TMAH solution (e.g., for separation from alkalis and alkaline earths), the feed volume containing the neptunium is loaded and left to stand in contact with the resin for 15-20 min before any rinsing or elution steps are begun.

IV. APPLICATION

Table IV, which is based on information in Table II, lists some column experiments, including a separation of Np(V) from U(VI) (item 5). The K_D of Np(V) in the combination of 0.5M citrate + 0.015M free tetramethylammoniumhydroxide is <20 ; for the same system on a pretreated column, that for U(VI) is greater than 200. Thorium(IV) is also retained

TABLE IV. Column Experiments Conducted on Basis of Information in Table II. Resin column size was 3.3 cm x 0.5-cm diameter (~0.33 g).

System ^a	pH	Metal	Concentration, total counts/min	Remarks
1. 0.5M Citrate + 0.015M TMAH	8	Np(V)	1.5×10^6	Peak elution before 10 ml; 95% elution in 35 ml.
2. 0.5M Citrate + 0.015M TMAH	8	U(VI)	5.7×10^5	Effluents showed background for first 40 ml, except for some sporadic counting possibility due to ^{233}U decay chain daughters. Uranium was found in top centimeter of column, indicating $K_D > 200$.
3. 0.5M Citrate + 0.015M TMAH	8	Th(IV)	5×10^6	No thorium detected in first 40 ml.
4. 0.5M Citrate + 0.015M TMAH	8	Pu(IV)	8×10^6	18% eluted after 25 ml.
5. 0.5M Citrate + 0.015M TMAH	8	Np(V) + U(VI)	$>10^6$	After 35 ml, 99% of the Np(V) was eluted. The ^{233}U was eluted with 0.5M HCl to give 98% of the original spike. This is a good material balance, the difference being made up possibly by decay chain daughters.
6. 0.5M Citrate + 0.03M TMAH	9	Np(V)	1.5×10^5	Peak elution ≤ 6 ml; 93% eluted in 26 ml.
7. 0.5M Citrate + 0.03M TMAH	9	U(VI)	5.7×10^5	40% eluted in 25 ml.
8. 0.1M Citrate + 0.5M TMA ⁺ CL ⁻	10	U(VI)	5.7×10^5	16% eluted in 20 ml; tailed off.
9. 0.1M Citrate + 0.5M TMA ⁺ CL ⁻	10	Np(V)	1.8×10^6	Peak elution at 10 ml; 80% eluted in 20 ml.
10. 0.9M TMAH + 0.1M Citrate	>10	U(VI)	1.1×10^6	Peak elution < 11 ml; 99.9% eluted in 25 ml; $K_D \approx 6$.
11. 0.9M TMAH + 0.1M Citrate	>10	Th(IV)	1.2×10^6	No thorium detected in first 20 ml.
12. 0.9M TMAH + 0.1M Citrate	>10	Pu(IV)	1.8×10^6	80% eluted in 20 ml, with peak eluted below 5 ml showing a large amount of tailing.

^aThe concentrations listed for TMAH represent the excess TMAH over that amount required to neutralize the organic acid (see Section II).

by the column past the total elution of Np(V) . The following serves as an example of the separation of neptunium from uranium. A small anion-exchange column (0.3 g) was treated successively with 1M TMAH, 0.1M TMAH, and a 0.5M citrate + 0.015M TMAH (pH 8) rinse. A spike of 100 λ of ^{233}U , equivalent to 1.12×10^6 counts/min, was taken down to dryness and picked up in 50 λ of a 1M TMAH solution containing 1.53×10^6 counts/min Np(V) . To lower the pH, 4 mg of solid citric acid was added, and the volume taken up to 0.5 ml with the 0.5M citrate + 0.015M TMAH. The total volume was loaded onto the column and eluted with 0.5M citrate + 0.015M TMAH, collecting 5-ml fractions. After 35 ml of elutriant passed through the column, >99% of Np(V) was eluted. The Np(V) fraction was found to contain no ^{233}U detectable by radiometric analysis. A subsequent elution with 0.5M HCl removed 98% of the uranium added. Thorium(IV) is also retained with the uranium and accompanies the latter during the 0.5M HCl elution. Uranium can be separated from thorium on an anion-exchange column in 0.1M citrate-0.9M free TMAH, where the K_D of the uranium is less than 6, that of the thorium being >100. Because of early breakthrough and excessive tailing, Pu(IV) is a hindrance in all these separations; thus, it would have to be handled by other means.

V. RECOVERY OF NEPTUNIUM

Two methods can be used to recover neptunium from the TMAH-citrate mixture.

1. To the basic TMAH-citrate solution containing Np(V) , Ba(OH)_2 solution can be added. An insoluble barium neptunate forms, and the neptunium is precipitated nearly quantitatively. The barium neptunate residue is washed and dissolved in dilute HCl. The barium can be separated from the neptunium by ion exchange or precipitation as BaSO_4 .

2. The TMAH-citrate effluent containing neptunium can be concentrated by evaporation and made 8M in HCl. The solution is then passed through an anion-exchange column, and the neptunium is retained. The citrate and TMA^+ ions are eluted with 8M HCl.

VI. DISCUSSION

Tables I-IV and Section IV indicate that a suitable separation for Np(V) from U(VI) and Th(IV) has been obtained, with Pu(IV) remaining as a major impurity, present in both fractions.

A somewhat qualitative explanation of the mechanism by which neptunium is eluted, and uranium is not, rests on the fact that when Ba(OH)_2 was added to citrate solution containing U(VI) and Np(V) , the neptunium

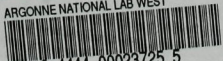
precipitated and the uranium remained in solution. Since barium precipitates $U(VI)$ in the absence of citrate under otherwise similar conditions, this would seem to indicate that a strong anionic citrate complex forms with uranium, and furthermore the neptunium may be displaced from the anion exchanger by a mass (OH^- , citrate) ion effect. Without further data concerning the structure in the feed solutions and effluents, nothing further can be said about the mechanism of separation. Equilibrium conditions were essentially obtained because the K_D values in batch and column work were generally comparable.

From this study it can be concluded that there is a separation of neptunium from uranium and thorium, as well as a separation of uranium from thorium. It is hoped that the information in Table II will be useful in determining other separations.

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